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"Fabrication and Characterization of Concentric-Tubular Composite Micro- and Nanostructures Using the Template-Synthesis Method"

by Veronica M. Cepak, John C. Hulteen, Guangli Che, Kshama B. Jirage, Brinda B. Lakshmi, Ellen R. Fisher & Charles R. Martin

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Colorado State University
Department of Chemistry
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6. Veronica M. Cepak, John C. Hulteen, Guangli Che, Kshama B. Jirage, Brinda B. Lakshmi, Ellen R. Fisher, and Charles R. Martin

7. Charles R. Martin, Department of Chemistry, Colorado State University, Fort Collins, CO 80523-1872

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13. Abstract: The template-synthetic method is a general approach for preparing tubular micro- and nanostructures. This method has been used to prepare micro- and nanostructures composed of metals, carbons, semiconductors, polymers, and Li^+-intercalation materials. This paper describes the use of the template method to prepare composite tubular micro- and nanostructures. These composite structures consist of an outer tubule of one material surrounding inner tubules of different materials. Chemical strategies used to prepare these composite tubular structures include electroless deposition of Au; electropolymerization of conductive and insulating polymers; electrodeposition of metals and semiconductors; graphitization of polymer precursors; chemical vapor deposition synthesis; and sol-gel synthesis.

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Fabrication and Characterization of Concentric-Tubular Composite Micro- and Nanostructures Using the Template-Synthesis Method

Veronica M. Cepak, John C. Hulteen, Guangli Che, Kshama B. Jirage, Brinda B. Lakshmi, Ellen R. Fisher, Charles R. Martin*

Department of Chemistry

Colorado State University

Fort Collins, CO 80523

*Corresponding author, via E-mail at crmartin@lamar.colostate.edu

ABSTRACT

The template-synthetic method is a general approach for preparing tubular micro- and nanostructures. This method has been used to prepare micro-and nanostructures composed of metals, carbons, semiconductors, polymers, and Li^+-intercalation materials. This paper describes the use of the template method to prepare composite tubular micro- and nanostructures. These composite structures consist of an outer tubule of one material surrounding inner tubules of different materials. Chemical strategies used to prepare these composite tubular structures include electroless deposition of Au; electropolymerization of conductive and insulating polymers; electrodeposition of metals and semiconductors; graphitization of polymer precursors; chemical vapor deposition synthesis; and sol-gel synthesis.

I. INTRODUCTION.

We have been investigating a general method for preparing tubular micro- and nanostructures called template synthesis.[1-4] This method entails synthesis of a desired material within the pores of a microporous membrane. The membranes employed have cylindrical pores with monodisperse diameters. A tubule or fibril of the desired material is obtained within each pore.

We have recently become interested in the idea of making concentric composite micro- and nanostructures of the type.[5] Such concentric tubular structures consist of an outer tubule of one material surrounding inner tubules of different materials. Such composites might have applications in microelectronics, chemical sensors, and electrochemical energy production. This paper describes synthetic strategies for preparing five different concentric-tubular micro- and nanostructures of this type. Synthetic methodologies used include electroless deposition of Au; electropolymerization of metals and semiconductors; graphitization of polymer precursors; chemical vapor deposition; and sol-gel synthesis. These methodologies were used to prepare composite tubules composed of metals, semiconductors, carbon, polymers, and Li^+-intercalating materials.

II. EXPERIMENTAL

A. Materials.

Polyester "track-etch" membranes with 1.0 μm, 2.0 μm, and 3.0 μm diameter pores were obtained from Poretics, and alumina membrane filters with 200 nm diameter pores were obtained from Whatman. Reagents for the electrochemical deposition of Au were used as received and have been reported in prior publications.[6, 7] Milli Q 18-MΩ water was used for rinsing and for all aqueous solutions.

Reagents used as received for the preparation and characterization of the Au/polyphenylene oxide (PPO)/polypyrrole (PPy) composite microstructures were 2,6-dimethylphenol (Aldrich), NaOH (Mallinkrodt), CF_3CO_2Na (Aldrich), $K_3Fe(CN)_6$ (Fisher), $NaIO_4$ (Fisher), KBr (FTIR grade, Aldrich), and methanol (ACS grade, Fisher). Pyrrole (Sigma) was distilled under N_2 prior to use. Reagents used as received for the preparation and characterization of the C/polyacrylonitrile (PAN)/Au composite nanostructures were $NH_4S_2O_4$ (Mallincrodt) and $NaHCO_3$ (Mallincrodt). The inhibitor was removed from acrylonitrile (Aldrich) by passing the monomer through a hydroquinone monomethyl ether disposable column (Aldrich).

Reagents used as received for the fabrication and characterization of TiS_2/Au composite microstructures were $TiCl_4$, 1-methyl-1-propanethiol, Li metal, and hexafluoroisopropanol (HFIP), and were all purchased from Aldrich. $LiClO_4$ (Aldrich) was dried under vacuum at 150° C for 24 hours to remove H_2O. Ethylene carbonate (Aldrich) and diethyl carbonate (Aldrich) were distilled prior to use. Al foil was used as received. Reagents used as received for the fabrication and characterization of TiO_2/Au composite microstructures were titanium (IV) isopropoxide (Aldrich), absolute ethanol (McCormick), 3-mercaptopropyltrimethoxysilane (Hüls), acetic acid (Mallinckrodt) and hydrochloric acid (Mallinckrodt). Reagents used as received for the fabrication and characterization of ZnO/Au composite microstructures were $ZnCl_2$ (Mallinckrodt), KCl (Mallinckrodt), and O_2 (General Air).

B. Electrochemical and other measurements.

Electrochemical depositions and cyclic voltammetry were done using a PAR Model 173 potentiostat in conjunction with a Yokogama 3025 x-y recorder. All solutions were purged with N_2 prior to and during measurements, except in the case of ZnO electrodeposition. Scanning electron micrographs were

obtained on a Phillips 505 microscope, and energy dispersive spectra were collected using a Kevex super 8000 microanalysis system equipped with a Li drifted Si detector.

FTIR spectra were obtained on a Galaxy 4021 spectrometer. The TiO_2 and C tubules were annealed using a Thermacraft model 2214 furnace. The O_2 plasma was formed using a Micro 85 Technics series 85 plasma system. DC conductivity measurements were taken using a Keithly 192 digital multimeter.

A home built CVD reactor, described elsewhere, was used for TiS_2 deposition.[8] Both the TiS_2/Au and TiO_2/Au microstructures were investigated using cyclic voltammetry with a CV-47 (BAS) voltammograph and an Omnigraphic x-y recorder. Cyclic voltammetry was done in a glove box filled with Ar. Powder XRD was obtained using a Enraf Nordas FR552 camera with a Cu K_α anode using 2–theta representation.

C. Fabrication of the Au/polyphenylene oxide/polypyrrole composite microstructures.

Polyester track-etch membranes (pore dia. = 3 μm, thickness = 10 μm) were used to prepare these composites. The outer Au tubule was deposited using an electroless plating method described previously.[6, 7] This method yields a Au microtubule within each pore; in addition, Au surface layers form on both faces of the membrane. One surface layer was removed from the Au plated membrane by polishing with a laboratory tissue dampened with methanol. The exposed Au tubules were used as anodes for electropolymerization of inner tubules of the polymer poly(2,6-dimethylphenol) (PPO).[9] This was accomplished by attaching a piece of conductive Cu tape to the remaining Au surface layer; this tape served as a working electrode contact. The Au membrane was clamped between a glass o-ring joint and a glass slide to form an electrochemical cell. A

Ag/AgCl reference electrode (BAS RE-5) and a spiral Pt wire electrode were also placed in this one compartment cell.

The electropolymerization of the inner PPO tubules was accomplished using cyclic voltammetry by scanning between the limits of - 0.2 V and + 0.8 V [9]. To ascertain that the inner PPO tubules had formed, cyclic voltammetric experiments were conducted at the Au tubule electrodes before and after PPO deposition. $K_3Fe(CN)_6$ (2 mM in 0.2 M NaO_2CCF_3) was used as the voltammetric probe. Oyama *et. al.* have shown that the PPO films are impermeable to this anion;[9] formation of the inner PPO tubules could, therefore, be ascertained by the disappearance of the $Fe(CN)_6^{3-/4-}$ voltammetric wave.

FTIR was used to confirm that the polymer deposited was PPO. The Au/PPO-tubule-containing membrane was placed in CH_2Cl_2 to dissolve any electropolymerized polymer. A small amount of KBr was added to this solution, and the mixture was heated in an oven at 100° C for several hours to remove the solvent. A KBr pellet was then made using a Carver laboratory press so that a FTIR spectrum of the electropolymerized PPO could be taken.

The final step was to deposit polypyrrole (PPy) microwires down the center of the inner PPO tubules. After PPO deposition, the Au/PPO-tubule-containing membrane was removed from the electrochemical cell. Both surfaces were cleaned with a damp laboratory tissue, and a new Au film was sputtered onto the bottom of the membrane. This Au film was used as the working electrode to electropolymerize the PPy microwires within the PPO tubules. The electrochemical cell described above was used; PPy was deposited into the PPO inner tubules using a constant current density of 0.14 mA cm^{-2}. The polymerization solution consisted of 0.1M pyrrole and 0.025 M $NaIO_4$ in 1:2 (v/v) methanol/H_2O. The completed Au/PPO/PPy composite microstructures within

the pores of the template membranes were analyzed using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).

D. Fabrication of carbon/polyacrylonitrile/Au composite nanostructures.

The alumina template membrane (200 nm-dia. pores) was used to prepare these composites. The outer graphitic carbon tubules were prepared by a previously-reported procedure; this method entails aqueous polymerization of acrylonitrile to make PAN tubules followed by thermal graphitization to make the corresponding carbon tubules.[10] The resulting C/alumina membrane was exposed to an O_2 plasma to remove the C surface layer. FTIR and DC conductivity measurements were used to confirm that C nanotubules were synthesized within the pores of the membrane.

The C/alumina membrane was then immersed into a fresh aqueous acrylonitrile polymerization solution (3 hours at 0° C). This caused inner PAN tubules to form within the previously-deposited C tubules. The membrane was again exposed to an O_2 plasma to remove the surface PAN layer. FTIR and conductivity measurements were again used to confirm that inner PAN tubules had been obtained.[10] Further characterization of these composite nanostructures using SEM involved dissolving the alumina membrane in NaOH before analysis.[10]

The final step to fabricate the C/PAN/Au composite nanostructures was the electrochemical deposition of Au nanowires within the inner PAN tubules. A Au film was sputtered onto one side of the C/PAN/alumina composite membrane to create a working electrode. An adhesive Cu tape contact was applied to the Au film, and this electrode was then sealed in epoxy. The Au nanowires were electrodeposited from a commercial plating solution (Orotemp 24, Technics). A constant cathodic current density of 2.0 mA cm^{-2} was applied until 2 coulombs of charge were passed. We have reported on this method to form template

synthesized metal microtubules previously.[11] DC conductivity measurements were used to confirm that the desired Au nanowires had been obtained. SEM was also used to characterize the composite nanostructures after dissolution of the alumina membrane.

E. Fabrication of TiS_2/Au composite microstructures.

The polyester template membrane with 1 μm-dia. pores was used to prepare these composites. The inner Au tubules were electrolessly deposited within the pores of the membranes,[6, 7] and one Au surface layer was removed by polishing with a wet cotton applicator stick. The resulting Au-microtubule-containing membrane was placed on a piece of Al foil with the intact Au surface layer down. This Al/Au/polyester composite sample was immersed in hexafluoroisopropanol (HFIP) overnight to dissolve the polyester. This left an ensemble of Au tubules standing upright from the Al foil surface. These tubules were placed within a chemical vapor deposition (CVD) reactor,[8] and TiS_2 tubules were deposited onto the outer surface of each Au tubule. The CVD reactor and TiS_2 synthesis are described elsewhere.[12] An atmosphere of 200 mTorr of $TiCl_4$ and 600 mTorr of 1-methyl-1-propanethiol was used in the CVD reactor.[13] The Al foil/Au tubule substrate temperature was 250° C, and the deposition time was between 2 and 3 minutes.

TiS_2 has been used as an electrode material in Li and Li-ion batteries.[14] Cyclic voltammetry in an inert atmosphere was used to explore the Li^+ intercalation electrochemistry of the outer TiS_2 tubules. Electrical contact was made to the TiS_2/Au composite microtubules through the Au surface layer on top of the Al foil. Li metal was used as the counter and reference electrodes.[12] The solvent consisted of a 3:7 (v/v) solution of ethylene carbonate and diethyl carbonate with 1 M $LiClO_4$.

F. Fabrication of TiO_2/Au composite microstructures.

The polyester membrane with 1 μm-dia. pores was used to prepare these composites. The outer Au tubules were electrolessly deposited inside the pores of the membrane.[6, 7] One of the surface Au layers was removed as described above, and the Au/polyester composite was placed (remaining surface layer down) on Al foil. The polyester was dissolved as described above. The exposed Au tubules, protruding from the Al foil surface, were immersed in a 2% solution of 3-mercaptopropyltrimethoxysilane in ethanol. The pH of this solution was adjusted to 5 with acetic acid. After two minutes, the sample was removed from the silane solution, washed in ethanol, and cured in an oven at 110° C for 10 minutes.

This ensemble of silylated Au tubules was dipped into a TiO_2 sol prepared as reported by Yoko *et. al.* [15, 16] This resulted in the deposition of the TiO_2 sol onto the outer surfaces of the Au tubules. The sample was transferred to a furnace for sintering at 450° C (sintering time = 3 hours). This yielded the desired outer TiO_2 tubules surrounding the inner Au tubules. These composite microstructures were analyzed by SEM and powder X-ray diffraction (XRD). As was the case with the TiS_2 tubules, cyclic voltammetry was used to explore Li^+ intercalation into the TiO_2 tubules.[17, 18] The reagents were the same as was used in the electrochemical characterization of TiS_2 tubules.

G. Fabrication of ZnO/Au composite microstructures.

The polyester membrane with 2 μm-dia. pores was used to prepare these composites. As before, the outer Au tubules were electrolessly deposited within the pores of the membrane.[6, 7] One Au surface layer was then removed, and the membrane was placed, remaining Au surface layer down, onto a piece of conductive Cu tape. The Cu tape was used as the working electrode contact. The membrane was then immersed into HFIP overnight to dissolve the polyester. As before, this left the Au tubules protruding upright in an array from the Cu tape

surface. These Au tubules were used as cathodes to deposit ZnO using the method reported by Lincot and Peulon.[19] The resulting ZnO/Au composite microstructures were washed with methanol and dried in an oven at 100° C. SEM and powder XRD were used to characterize these microstructures.

III. RESULTS AND DISCUSSION

A. Au/PPO/PPy composites microstructures.

These composite microstructures were synthesized in the rather large (3 μm-dia.) pores of the polyester template membrane so that the structures obtained after each synthetic step could be clearly imaged with a scanning electron microscope (Figure 1). As discussed above, these composite microstructures were prepared using a combination of electroless Au plating followed by electropolymerization of poly(2,6-dimethylphenol) (PPO), followed by electropolymerization of polypyrrole (PPy).

The outer Au tubules obtained after the electroless deposition step are shown in Figure 1B. Inner tubules of PPO were then electropolymerized within these Au tubules (Figure 1C). A cyclic voltammetric experiment was used to confirm the presence of the inner PPO tubules. Prior to deposition of the inner PPO tubules, the Au tubule-containing membrane was immersed into an aqueous solution of $Fe(CN)_6^{3-}$. The characteristic $Fe(CN)_6^{3-/4-}$ voltammetric wave is clearly discernible (Figure 2). This indicates that the Au tubule electrodes are conductive and accessible to the aqueous solution. After deposition of the PPO inner tubules, $Fe(CN)_6^{3-}$ electrochemistry is not observed (Figure 2), indicating that the inner PPO tubules have completely covered all of the Au tubule surfaces.

This electrochemical experiment, along with the micrograph in Figure 1C, confirms that insulating and defect-free polymeric tubules had been deposited within the Au tubules. FTIR was used to confirm that the inner tubules were

comprised of PPO. As indicated in Figure 3, spectra obtained from the dissolved inner tubule material showed a prominent OH stretch at 3433 cm^{-1}, a CO stretch at 1267 cm^{-1}, and methyl CH stretches at 2958 cm^{-1}, 2928 cm^{-1}, and 2852 cm^{-1}.

The final step to produce the desired Au/PPO/PPy composite microstructures involved the electropolymerization of PPy microwires down the centers of the PPO tubules. PPy was electrochemically deposited from an aqueous/methanol solution containing $NaIO_4$ as the supporting electrolyte. The IO_4^- is incorporated as the dopant for the PPy. Electropolymerization was continued until the PPy microwires had propagated throughout the entire 10 μm thickness of the template membrane (Figure 1D). The IO_4^- anion, incorporated into the PPy microwires, was used as a chemical tag in energy dispersive spectroscopic analysis (EDS) to confirm that $PPyIO_4$ had, indeed, been deposited. EDS of this sample showed peaks at 3.9 keV and 4.2 keV which are the $L_{\beta 1}$ and $L_{\alpha 1}$ emissions of iodine (Figure 4). The peak at 2.1 keV is due to the $M_{\alpha 1}$ emission of Au.

As indicated in Figure 1, the resulting composite microstructures can be left within the pores of the template membrane. Alternatively, the template membrane can be dissolved to free the composite microstructures. The freed microstructures can then be collected by filtration. Figure 5 shows a micrograph of Au/PPO/PPy microstructures obtained in this fashion.

B. C/PAN/Au composite nanostructures.

An alternative set of chemistries was used to prepare this second insulator/conductor/insulator composite in the much smaller pores (200 nm dia.) of the alumina template (Figure 6A). A FTIR spectrum of the alumina template membrane before deposition of the outer PAN tubules is shown in Figure 7A. An analogous spectrum after polymerization of the PAN tubules (Figure 7B) shows a strong CN stretch at 2345 cm^{-1}. A two-point conductivity measurement across

the template membrane gave a PAN tubule conductivity of less than 10^{-9} S cm^{-1}. This indicates, as expected, that the PAN nanotubules were electronically insulating.

These PAN nanotubules were then subjected to a series of heat treatment procedures to convert them into nanotubules of a cyclized quasi-graphitic structure.[10] After the heat treatment procedures, the CN stretch disappears in the FTIR spectrum, indicating that cyclized C was formed (Figure 7C). The resulting C tubules (see Figure 6B) had a conductivity of 2×10^{-6} S cm^{-1}. This conversion to a semiconducting material indicates that partial graphitization of the PAN nanotubules had occurred. We have since developed procedures that provide conductivities as high as 0.01 S cm^{-1} for such graphitic tubules.[20]

After synthesizing the C nanotubules, a second PAN polymerization was done within the C-nanotubule-containing membrane to form inner nanotubules of PAN within each outer C nanotubule (Figure 6C). A careful comparison of the micrographs in Figure 6B and 6C shows that after the second PAN polymerization, the nanotubules have a slightly larger wall thickness. This increase in thickness indicates that thin PAN nanotubules had deposited onto the inner walls of the C nanotubules. FTIR was used to confirm the presence of these PAN nanotubules; note the return of the CN stretch in Figure 7D. The conductivity measured across the C/PAN nanotubule-containing membrane was again less than 10^{-9} S cm^{-1}, indicating that the outer semiconducting C tubules had been completely coated by the inner insulating PAN tubules.

Finally, Au nanowires were electrodeposited into the inner PAN nanotubules to complete the C/PAN/Au composite nanostructures (Figure 6D). The presence of the Au nanowires within these nanostructures was confirmed by again measuring the electrical conductivity across the thickness of membrane. A

conductivity of greater than 10^4 S cm^{-1} was obtained. This indicates that the Au nanowires, do indeed, extend throughout the entire thickness of the membrane.

C. TiS_2/Au composite microstructures.

Chemical vapor deposition (CVD) is another synthetic tool which can be used to prepare tubular composite microstructures. To illustrate the use of this synthetic method, CVD was used to deposit outer tubules of TiS_2 onto template-prepared inner Au tubules. The inner Au tubules (Figure 8A) were obtained via electroless Au deposition within the 1 μm dia. pores of a polyester membrane. The outer TiS_2 tubules were deposited using a CVD procedure involving the precursors, $TiCl_4$ and 1-methyl-1-propanediol.[8] The scanning electron micrographs (SEM) image in Figure 8B clearly show the TiS_2 deposited on the outer surfaces of the Au microtubules. Powder X-ray diffraction was used to confirm that the material deposited is TiS_2. X-ray diffraction data (Figure 9) show peaks at 34° and 54° 2θ which corresponds to the (110) and (101) reflections for hexagonal TiS_2 . The reflections at 38 and 44 2θ are from the Au tubules and the Al foil substrate, respectively.

One potential application of these TiS_2/Au composite microstructures involves their use as Li and Li-ion battery electrodes. TiS_2 has previously been used as an electrode material in these types of batteries.[14] We have recently shown that electrodes composed of template-synthesized Li^+-intercalating nanostructures provide higher discharge capacities than conventional electrodes prepared from the same material.[21] However, one potential problem with this new nanomaterial-based approach for preparing Li-ion battery electrodes concerns the low electrical conductivities of many of the Li^+-intercalation materials.[21] The CVD-based TiS_2/Au composite microstructure should solve this problem. This is because each outer TiS_2 tubule is coated onto its own current-collecting electrode (the inner Au tubule).

Figure 10 demonstrates this concept of using the inner Au tubules as current collectors for the outer TiS_2 tubules. Cyclic voltammetry was used to drive the reversible Li^+ intercalation reaction shown in Equation 1.

$$TiS_2 + x\ e^- + X\ Li^+ \text{------>} Li_xTiS_2 \qquad (1)$$

The voltammogram in Figure 10 shows that Li^+ is reversibly inserted and removed from the outer TiS_2 tubules. We are currently investigating the charge/discharge kinetics and capacities of such tubular composite battery electrode materials.[12]

D. TiO_2/Au composite microstructures.

We have recently shown that sol-gel chemistry can be used to deposit TiO_2, and other semiconducting oxide nanotubules, within the pores of alumina template membranes.[22] However, these TiO_2 nanotubules have low electrical conductivities. Because of this low conductivity, these nanotubules could not be successfully used as electrodes in Li and Li-ion batteries. As discussed above, by depositing each TiO_2 nanostructure onto its own current-carrying electrode (an inner Au tubule), this problem of low electrical conductivity can be circumvented. The TiO_2/Au composite microstructures prepared here illustrates this point.

Electrolessly deposited Au tubules (1 μm dia., Figure 11A) were treated with 3-mercaptopropyltrimethoxy silane. The thiol chemisorbs to the Au tubules, providing three surface $-OCH_3$ groups per chemisorbed -SH. These surface $-OCH_3$ groups help initiate growth of the subsequently-deposited sol-gel TiO_2 film.[23, 24] An electron micrograph of the composite microstructures after sol-gel synthesis of the outer TiO_2 is shown in Figure 11B. Because the outer TiO_2 tubules have such thin walls, it is difficult to see these tubules in the micrograph. Powder X-ray diffraction was used to confirm the presence of the TiO_2 tubules. X-ray diffraction data shows one intense peak at 25° 2θ which is due to the (101) reflection of TiO_2 anatase (Figure 11C). No other reflections can be seen due to

the strong background reflection of the Au tubules (at 38° 2θ). This data shows that outer anatase TiO_2 tubules of the anatase form had, indeed, formed on the inner Au tubules.

Cyclic voltammetry was used to further confirm the presence of the outer TiO_2 tubules. As before, cyclic voltammetry was used to drive reversible Li^+ intercalation (Equation 2) into these outer TiO_2 tubules.

$$TiO_2 + x\ Li^+ + x\ e^- \text{ ---> } Li_xTiO_2 \qquad (2)$$

Li^+ is known to intercalate into the anatase form of TiO_2 readily, but the extent of intercalation into other crystal forms, such as rutile or brookite, is usually reported as negligible.[18] Therefore, cyclic voltammetry can be used to verify that the TiO_2 tubules are of the anatase form. The cyclic voltammogram in Figure 11D clearly demonstrates that Li^+ rapidly and reversibly intercalated into the outer TiO_2 tubules. This voltammogram is also similar to voltammograms reported for single-crystal anatase[18] and for nanocrystalline TiO_2 films.[17] Further investigation of these TiO_2/Au composite microstructures for possible battery applications will be reported elsewhere.

E. ZnO/Au composite microstructures.

Finally, electrochemical deposition of a semiconducting material can also be used to prepare composite microstructures. Au tubules were first electrolessly deposited within the 2 μm dia. pores of the polyester template. The polyester was then dissolved to yield an ensemble of the Au tubules (Figure 12A). These tubules were then used as electrodes to deposit outer tubules of ZnO. The outer ZnO tubules were electrodeposited according to Equation 3 at a constant potential of 0.86 V vs. Ag/AgCl.

$$Zn^{2+} + 1/2\ O_2 + 2\ e^- \text{ ---> } ZnO \qquad (3)$$

As indicated in the micrograph in Figure 12B, ZnO particles are electrodeposited onto the outer surfaces of the Au tubule cathodes. By

controlling the deposition time, the thickness of the outer ZnO tubules layer can be varied. The powder X-ray diffraction pattern of these ZnO/Au composite microstructures shows 3 main peaks at 32°, 34°, and 36° 2θ (Figure 12C). These peaks are assigned to the (100), (002), and (101) reflections for hexagonal ZnO.

IV. CONCLUSIONS

We have shown that a broad arsenal of chemical synthetic methodologies, in combination with the template method, can be used to fabricate a large variety of composite micro- and nanostructures. The methodologies used here include electroless plating of metals; electrodeposition of insulating polymers, conductive polymers, semiconducting oxides, and metals; chemical vapor deposition; sol-gel chemistry; chemical polymerization; and graphitization. The micro- and nanostructures obtained are composed of different conducting, insulating, semiconducting, and electroactive materials. We are currently investigating potential applications of these composite micro- and nanostructures.

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FIGURE CAPTIONS

Figure 1. Scanning electron micrographs of the surface of the polyester template (A) and of the tubular structures obtained after each synthetic step in the preparation of the Au/PPO/PPy composite microstructures (B,C,D). (B) Surface of the template after electroless deposition of the Au tubules within the pores. (C) Surface of the template membrane after electropolymerization of PPO tubules within the Au tubules. (D) Surface of the template after electropolymerization of the polypyrrole microwires within the PPO tubules.

Figure 2. Cyclic voltammograms at the Au tubule electrodes (inside the polyester template membrane) before (A) and after (B) electropolymerization of the inner PPO tubules (scan rate = 50 mv s^{-1}). The solution was 2 mM $K_3Fe(CN)_6$ in 0.2 M NaO_2CCF_3.

Figure 3. FTIR spectra of electropolymerized PPO which was dissolved from the Au/PPO membrane.

Figure 4. Energy dispersive spectra before and after electropolymerization of the PPy microwires into the Au/PPO tubules. After PPy electropolymerization, two additional peaks appear in the EDS which have been identified as iodine emission peaks of the dopant IO_4^-.

Figure 5. Scanning electron micrograph of individual Au/PPO/PPy composite microstructures that were obtained by dissolving the polyester template membrane.

Figure 6. Scanning electron micrographs of the surface of the alumina template (A) and of the tubular structures obtained after each step of the synthetic procedure used to prepare the C/PAN/Au composite nanostructures (B,C,D). (B) The C tubules obtained after dissolution of the the template. (As noted in the text, the C/PAN/Au composites were prepared by doing the appropriate chemistries in sequence leaving the alumina template intact; however, it is easier

to image these extremely small structures after dissolving the template.) (C) As per (B), but after polymerization of a PAN tubule within each C tubule. Note that the PAN caused the tubule wall to be thicker than in Figure 6B. (D) After electrodeposition of a Au nanowire within each C/PAN nanotubule.

Figure 7. FTIR spectra of the CN stretching region of the C/PAN/Au nanocomposite at various stages of composite nanostructure formation. (A) An alumina template membrane. (B) After the first polymerization of acrylonitrile. (C) After the graphitization of the PAN tubules in (B). (D) After the second PAN polymerization.

Figure 8. Scanning electron micrographs of an ensemble of Au tubules before (A) and after (B) CVD of the outer TiS_2 tubules. The template membrane was dissolved away to allow the tubules to protrude from the substrate Au surface layer.

Figure 9. Powder x-ray diffraction data from the TiS_2/Au composite microstructures.

Figure 10. Cyclic voltammogram of TiS_2/Au composite microstructures indicating reversible Li^+ intercalation (scan rate = 0.3 mV s^{-1}). The electrolyte was 1M $LiClO_4$ in a 3:7 (v/v) solution of ethylene carbonate and diethyl carbonate.

Figure 11. Scanning electron micrographs of an ensemble of Au tubules before (A) and after (B) sol-gel deposition of TiO_2 onto the outer surfaces of the Au tubules. (C) Powder X-ray diffraction of the TiO_2/Au composite microstructures. (D) The material deposited, TiO_2 (anatase), was confirmed by Li^+ intercalation using cyclic voltammetry (scan rate = 0.3 mV s^{-1}, electrolyte as per Figure 10).

Figure 12. Scanning electron micrographs of an ensemble of Au tubules before (A) and after (B) electrochemical deposition of ZnO onto the outer tubule walls. The tubules are protruding from a Au surface layer mounted on Cu tape. (C) Powder x-ray diffraction pattern of these ZnO/Au composite microstructures.

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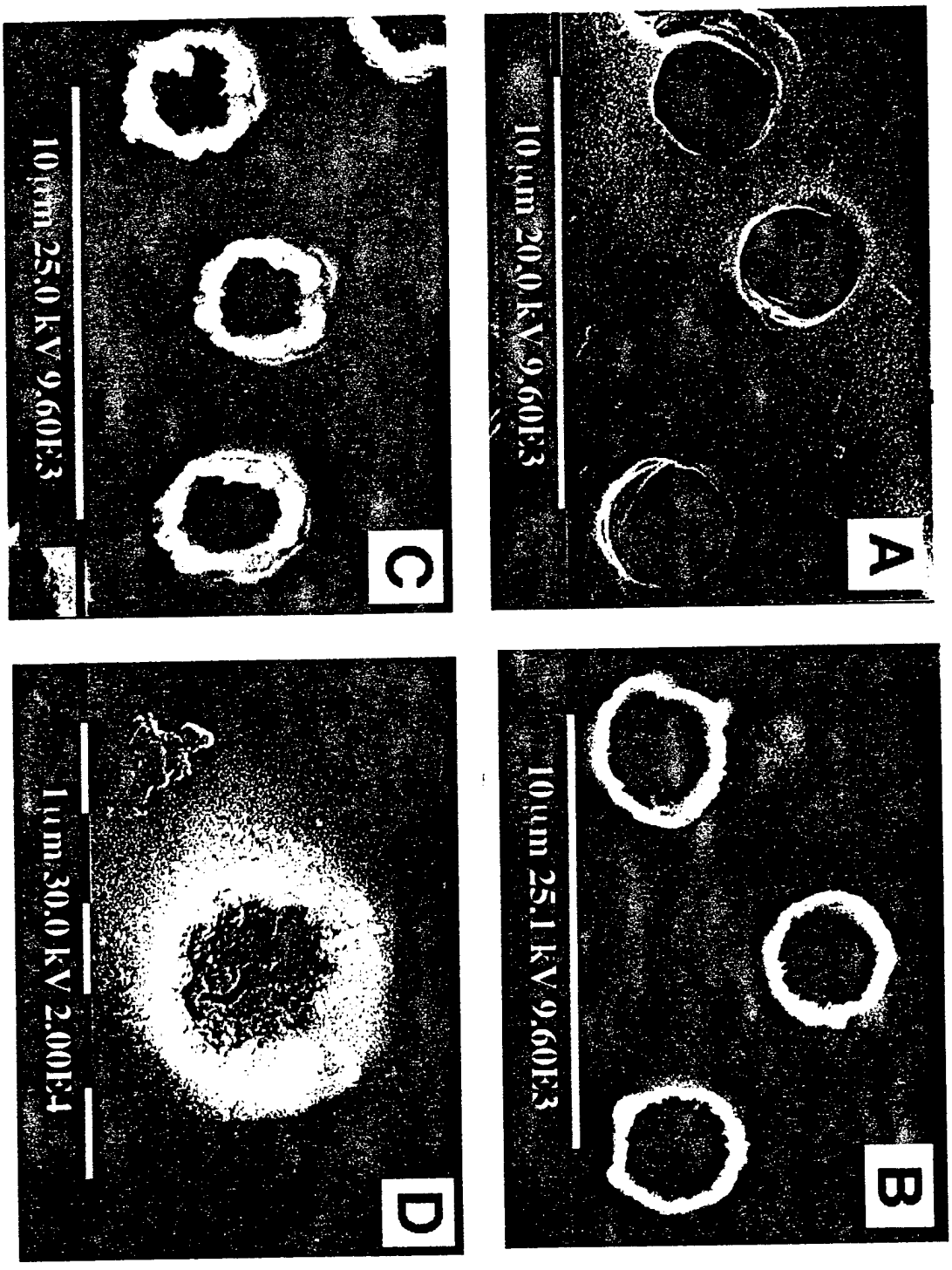

A
10 µm 20.0 kV 9.60E3
B
10 µm 25.1 kV 9.60E3
C
10 µm 25.0 kV 9.60E3
D
1 µm 30.0 kV 2.00E4

Fig 1

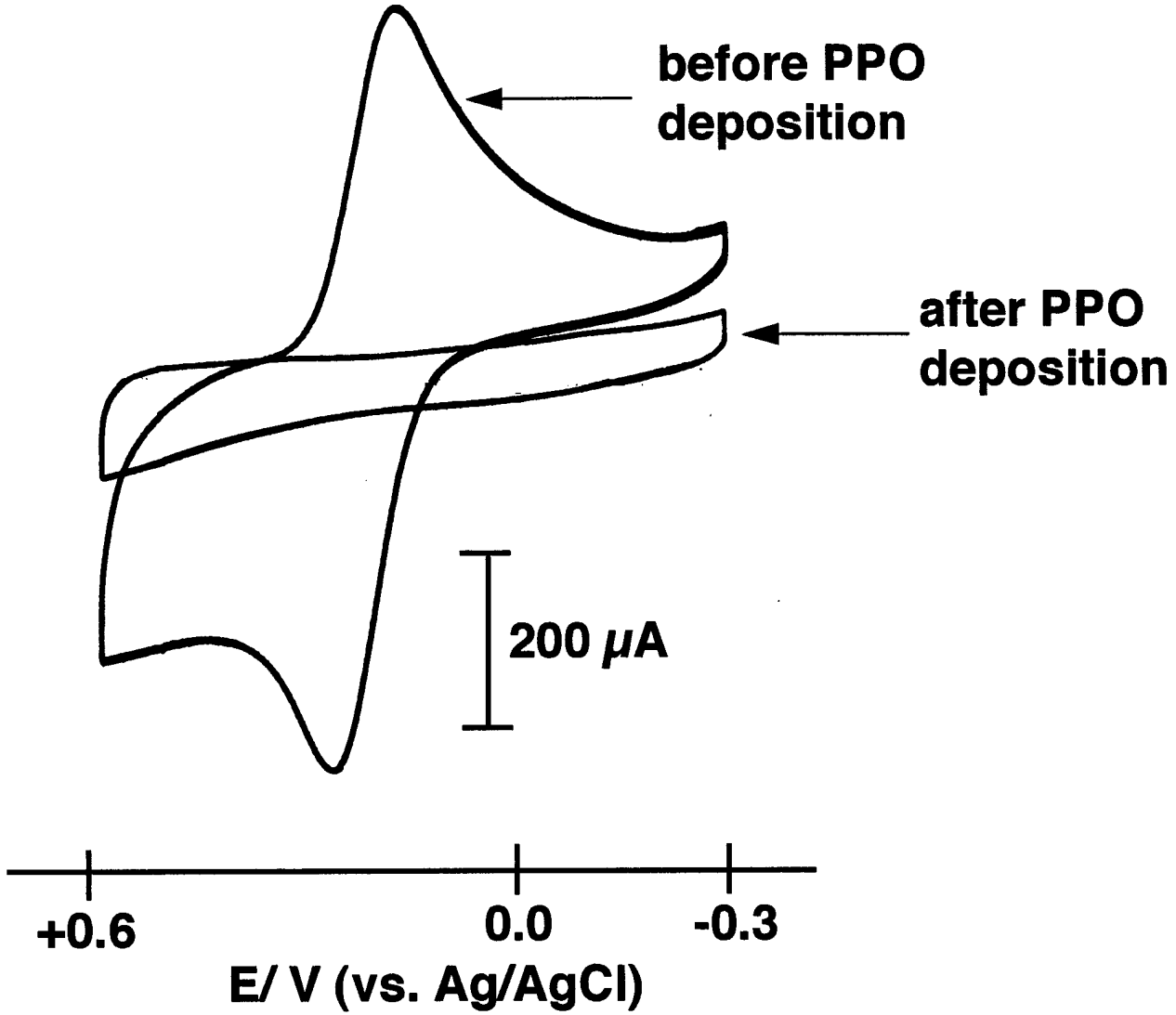

before PPO
deposition
after PPO
deposition
200 μA
+0.6
0.0
-0.3
E/ V (vs. Ag/AgCl)

Fig 2

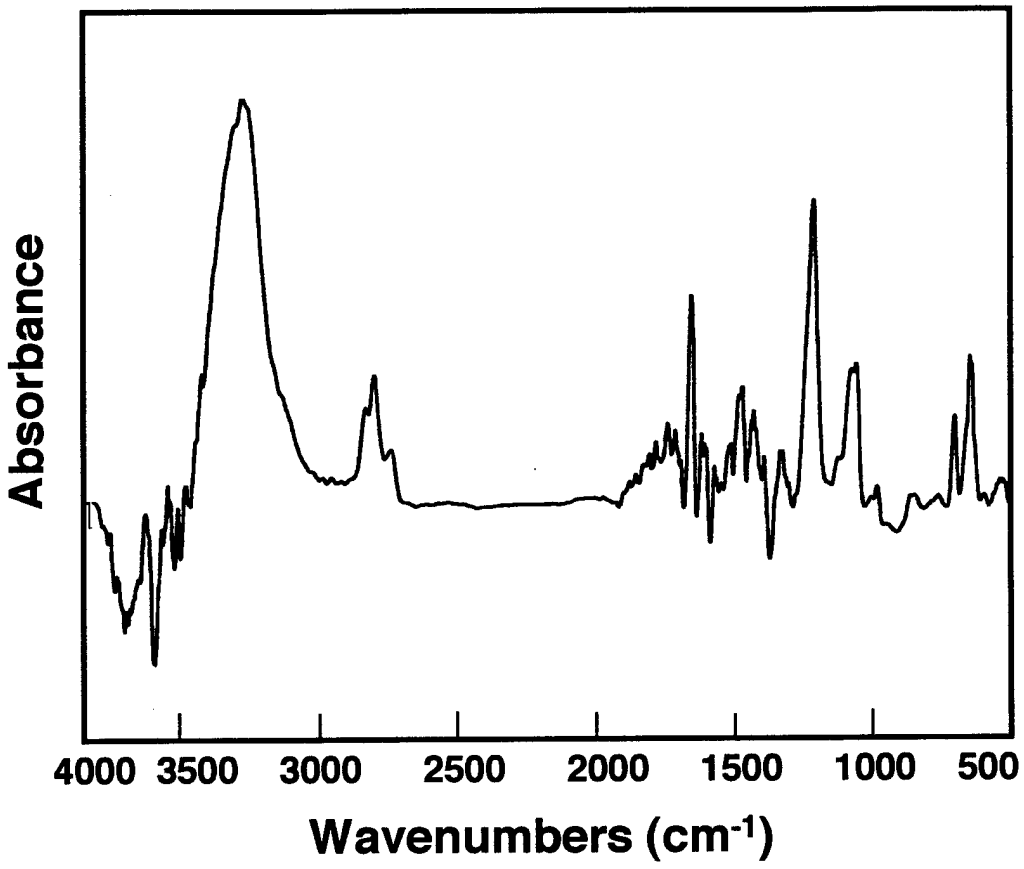

Absorbance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

Fig 3

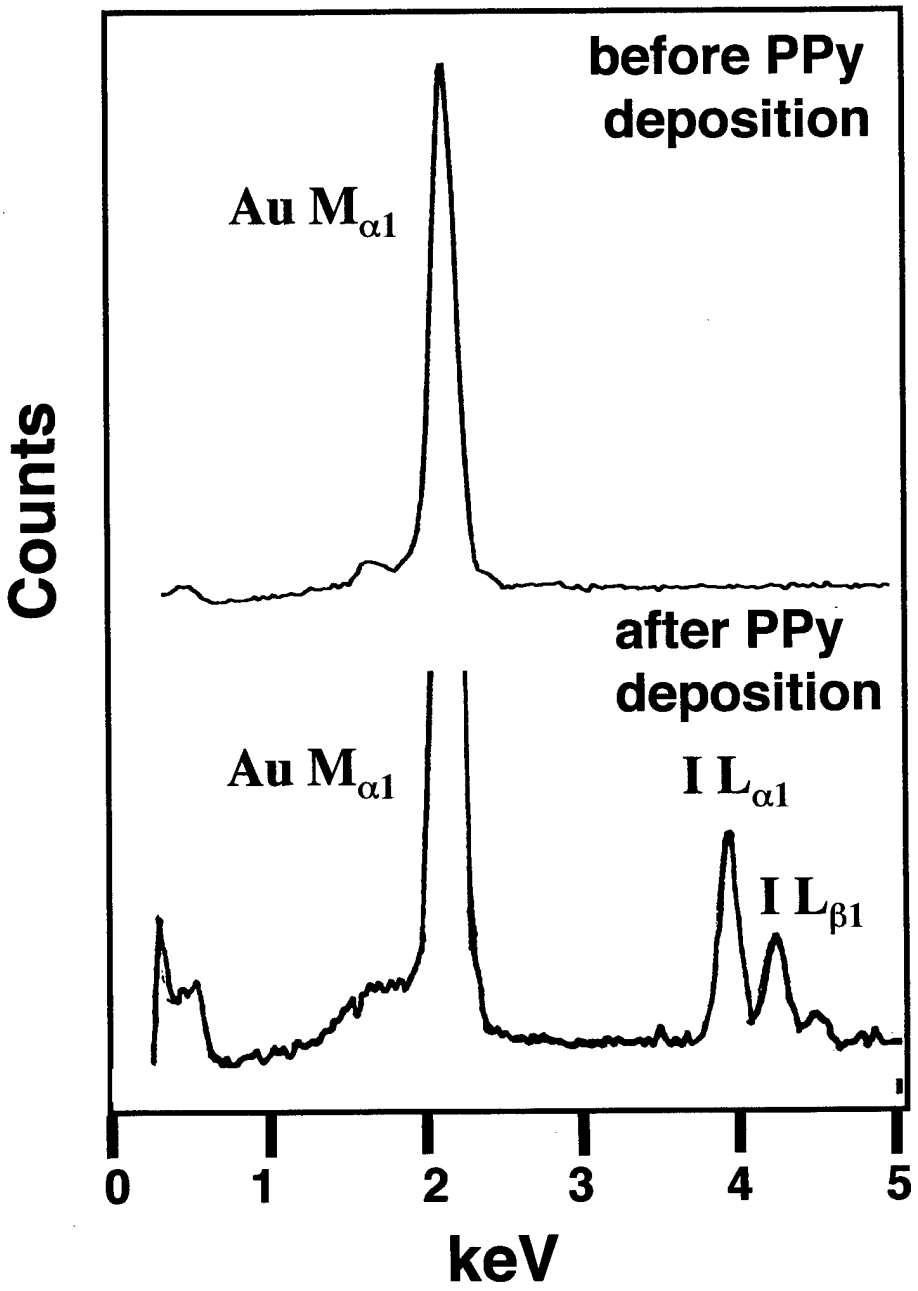

before PPy deposition
Au $M_{\alpha 1}$
Counts
after PPy deposition
Au $M_{\alpha 1}$
I $L_{\alpha 1}$
I $L_{\beta 1}$
0
1
2
3
4
5
keV

Fig 4

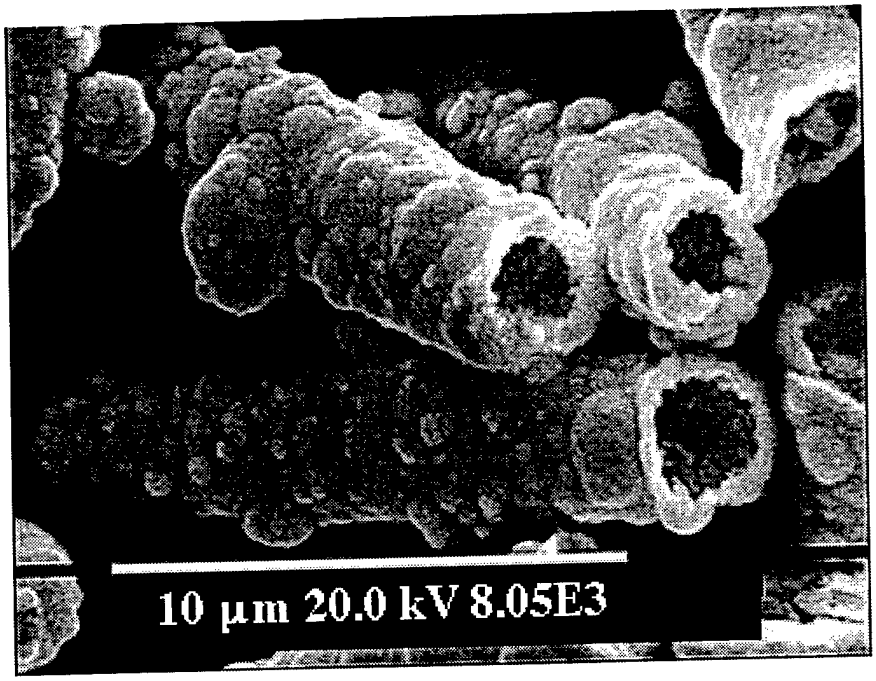


Fig 5

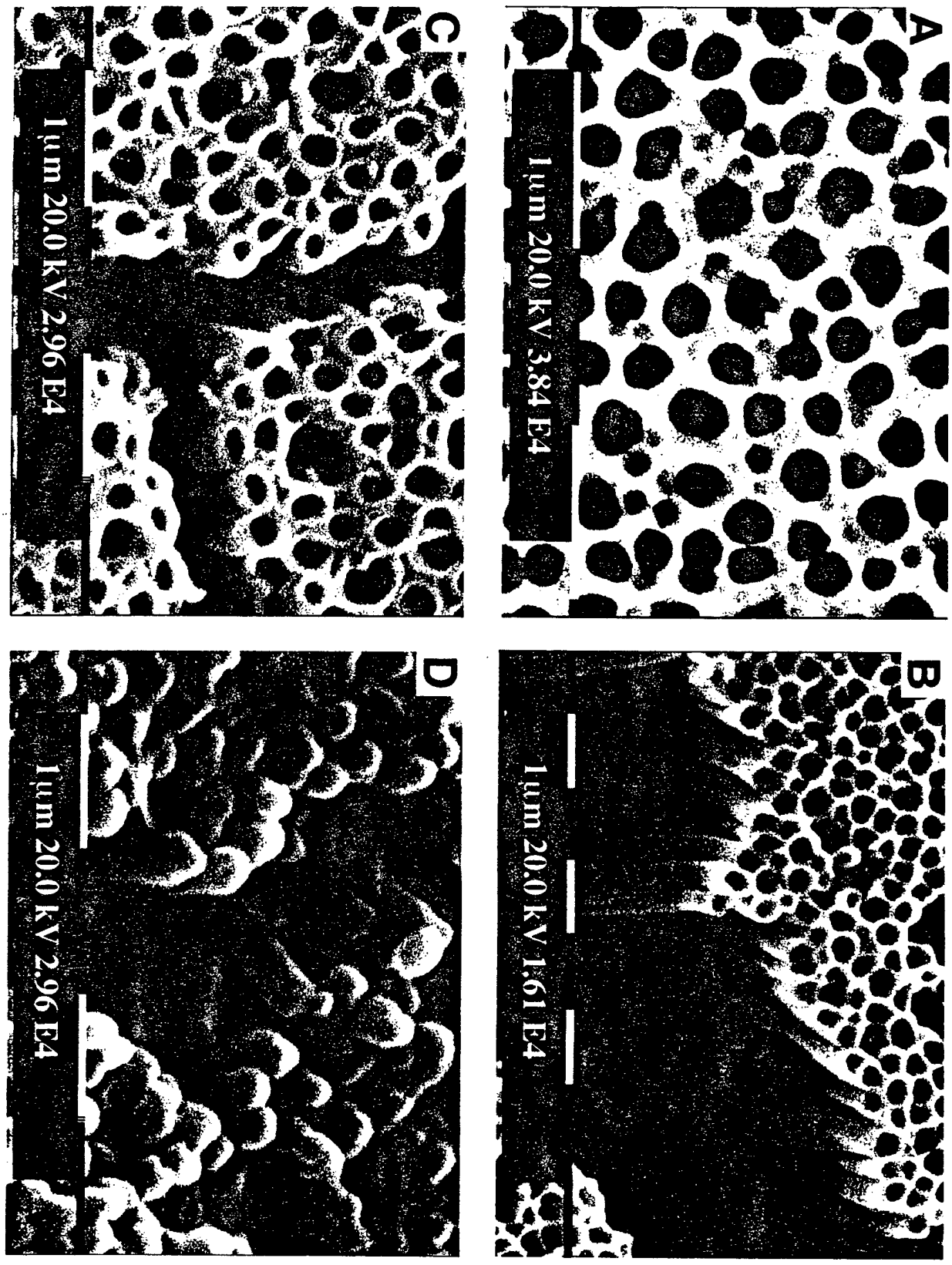

A
1 μm 20.0 kV 3.84 E4
C
1 μm 20.0 kV 2.96 E4
B
1 μm 20.0 kV 1.61 E4
D
1 μm 20.0 kV 2.96 E4

Fig 6

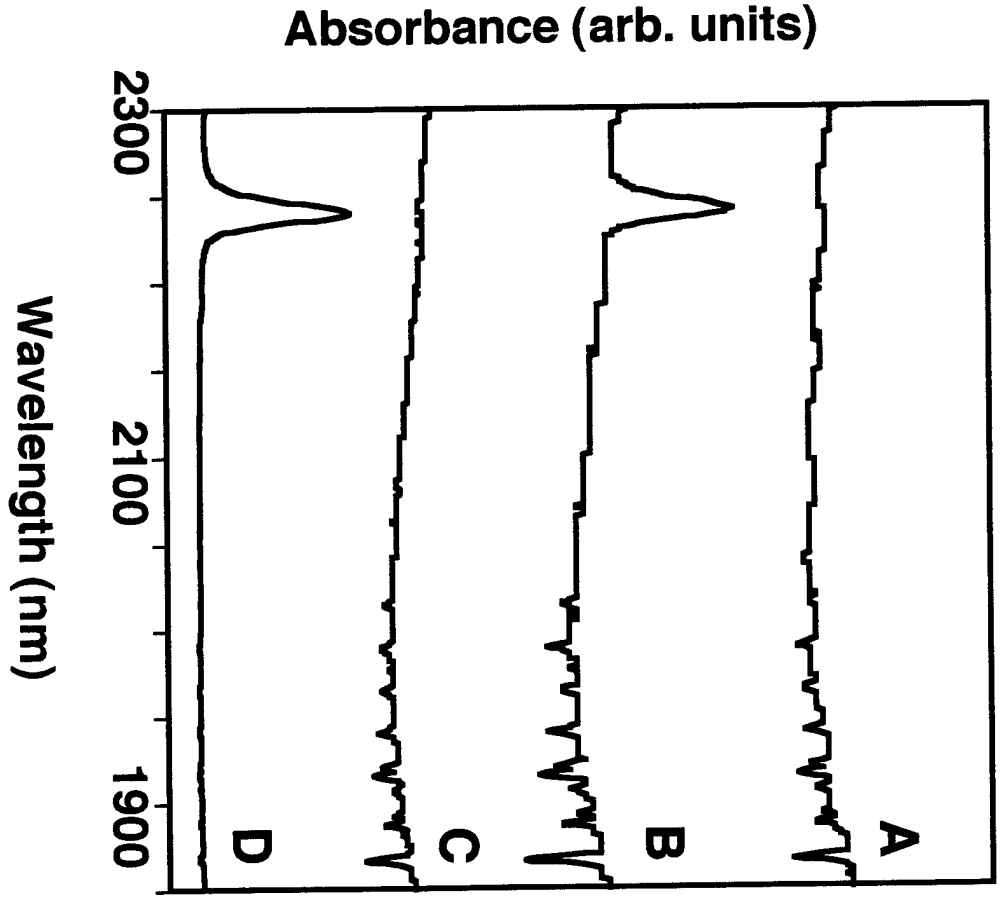
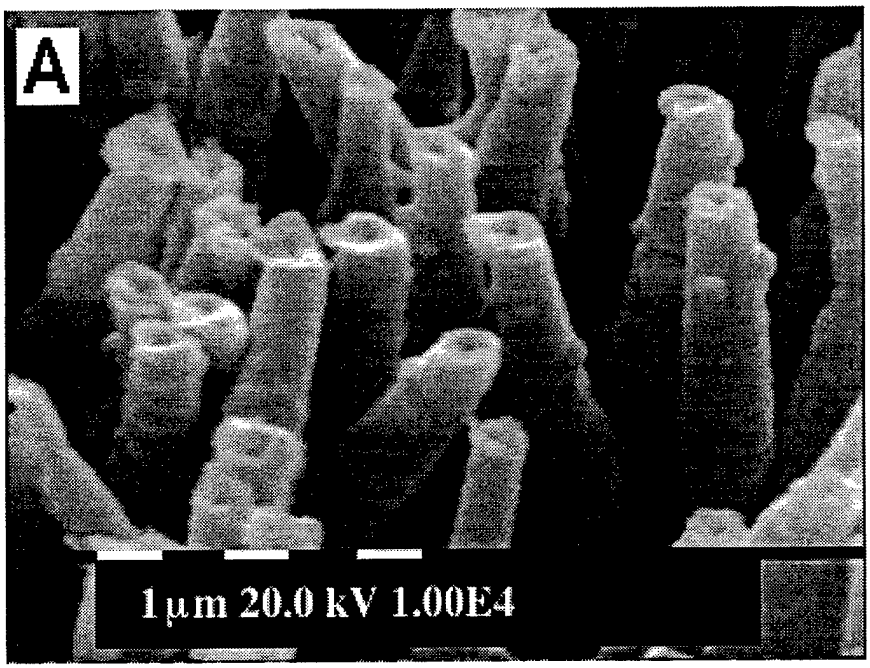


Fig 7



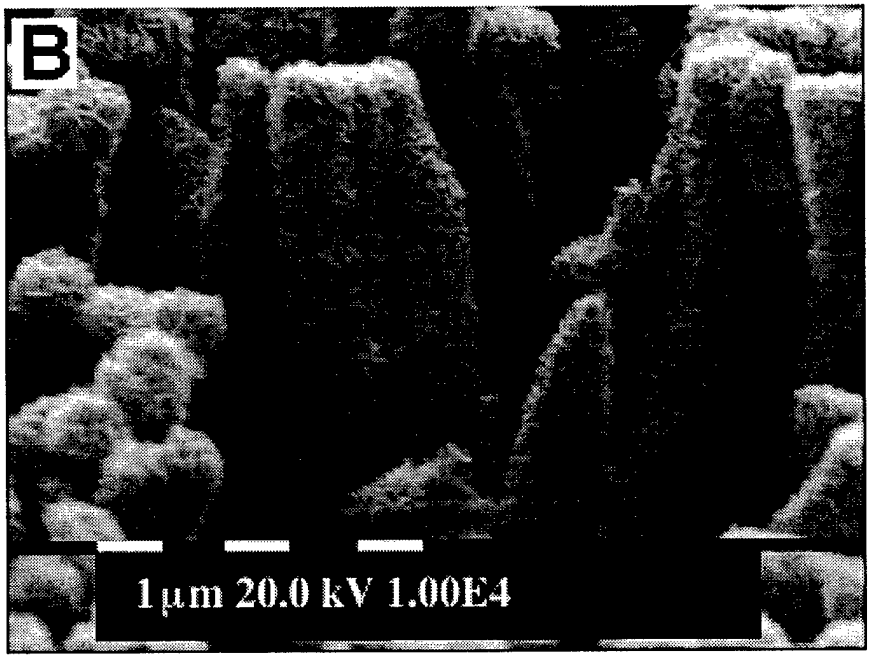


Fig 8

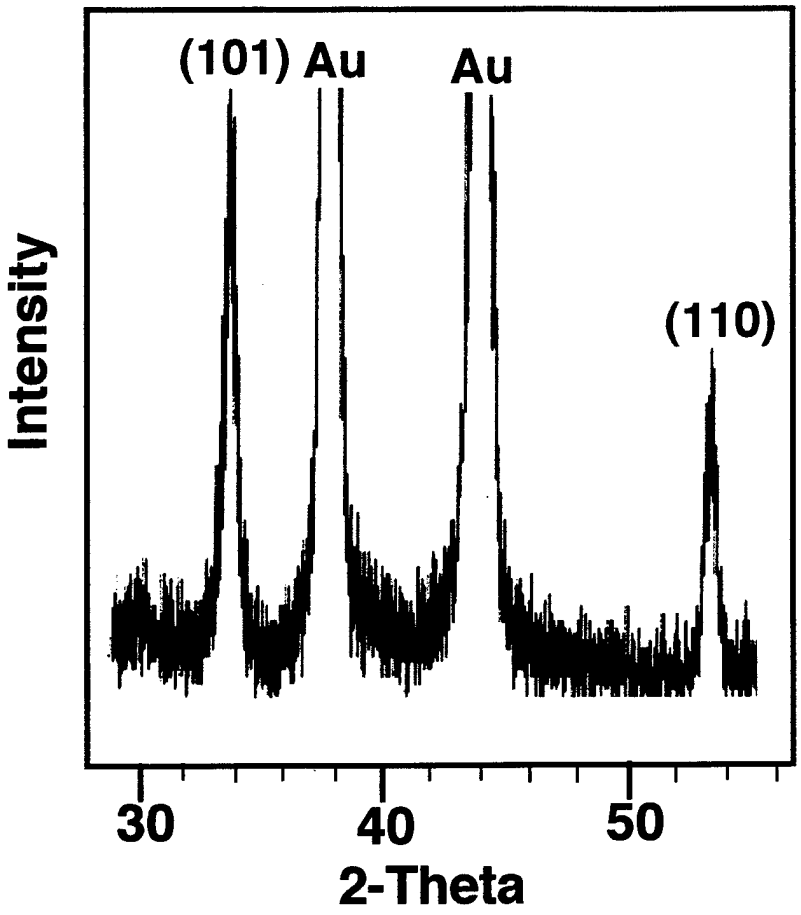


Fig 9

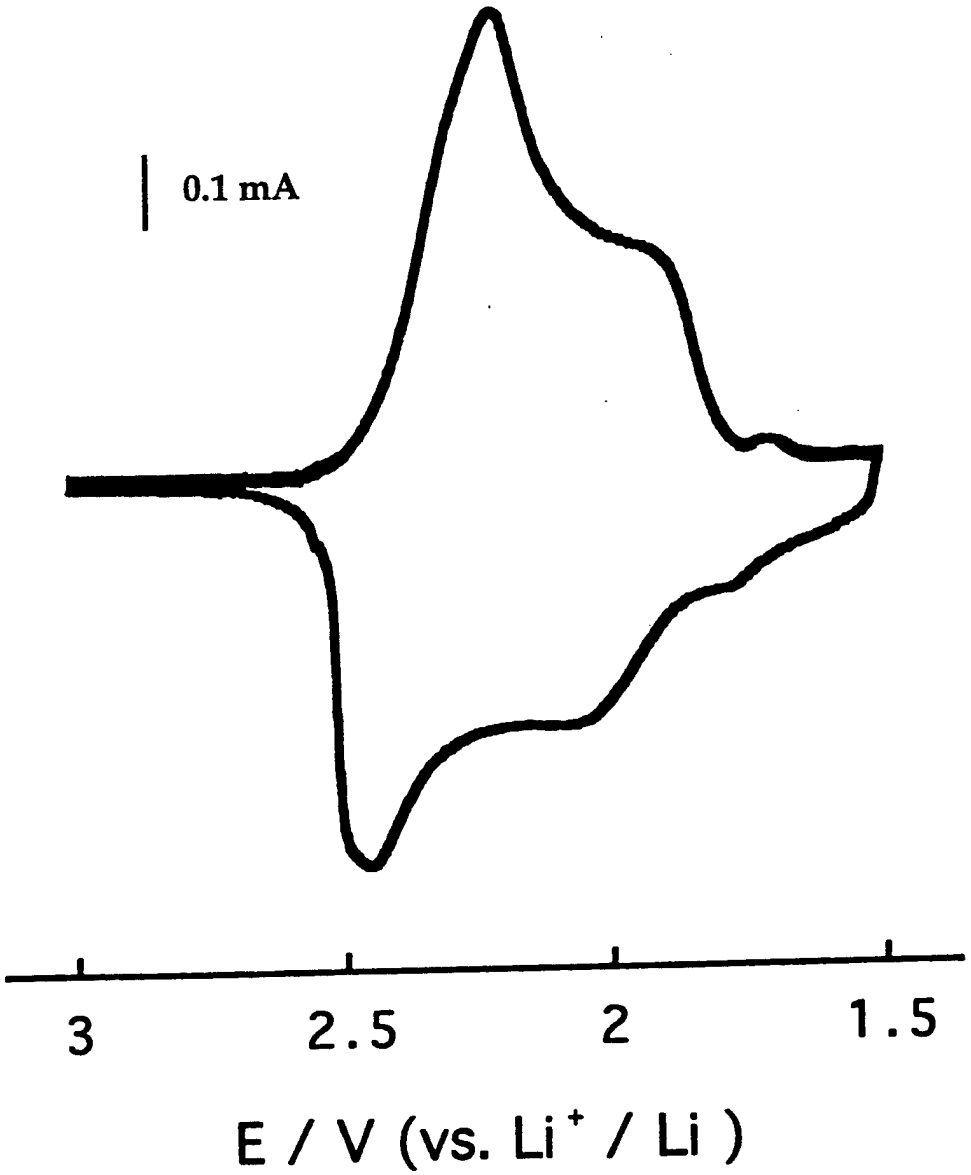
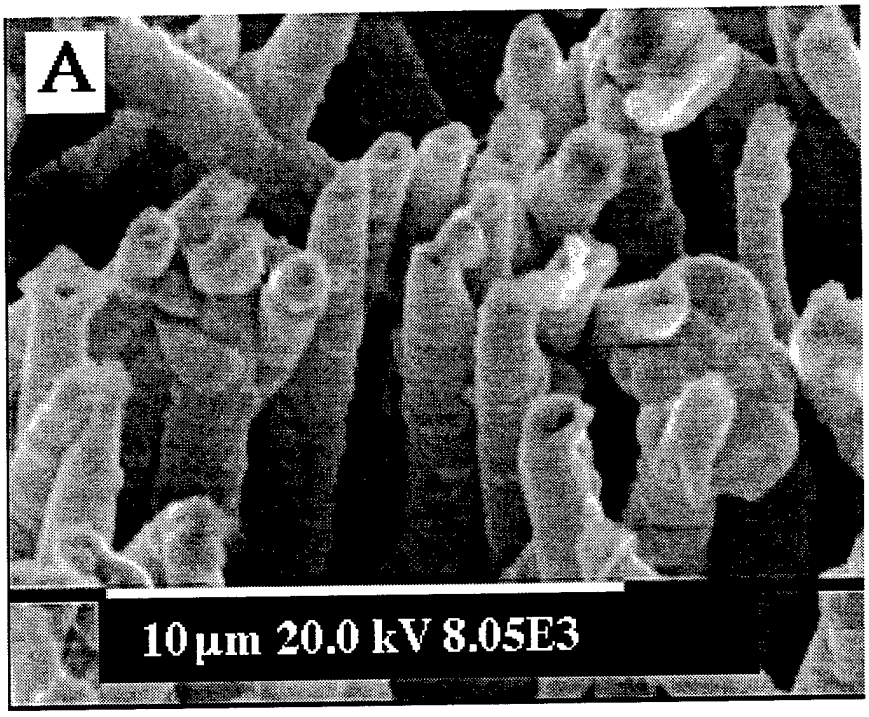


Fig 10



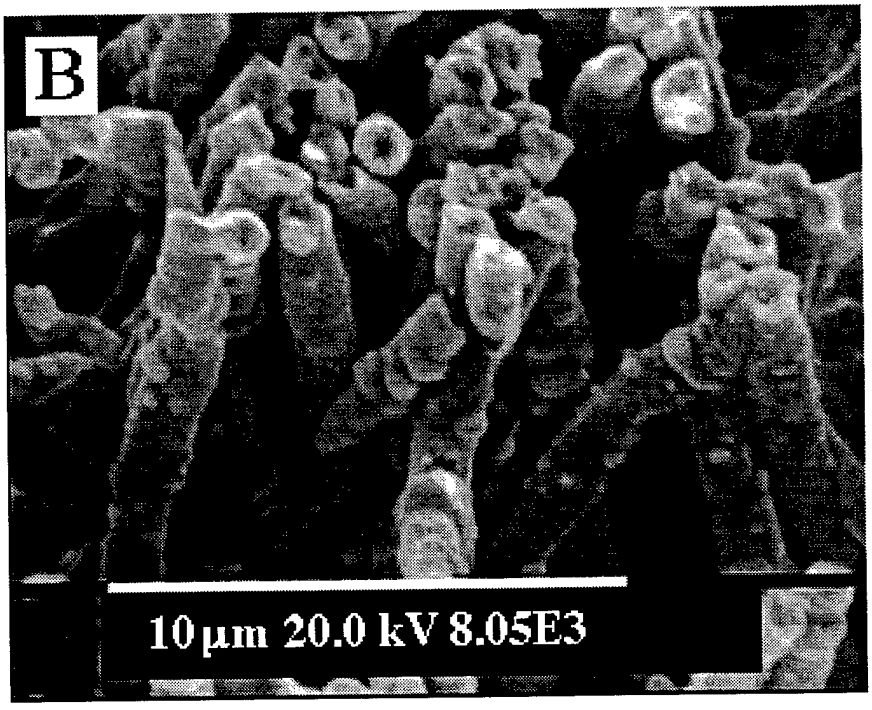


Fig 11

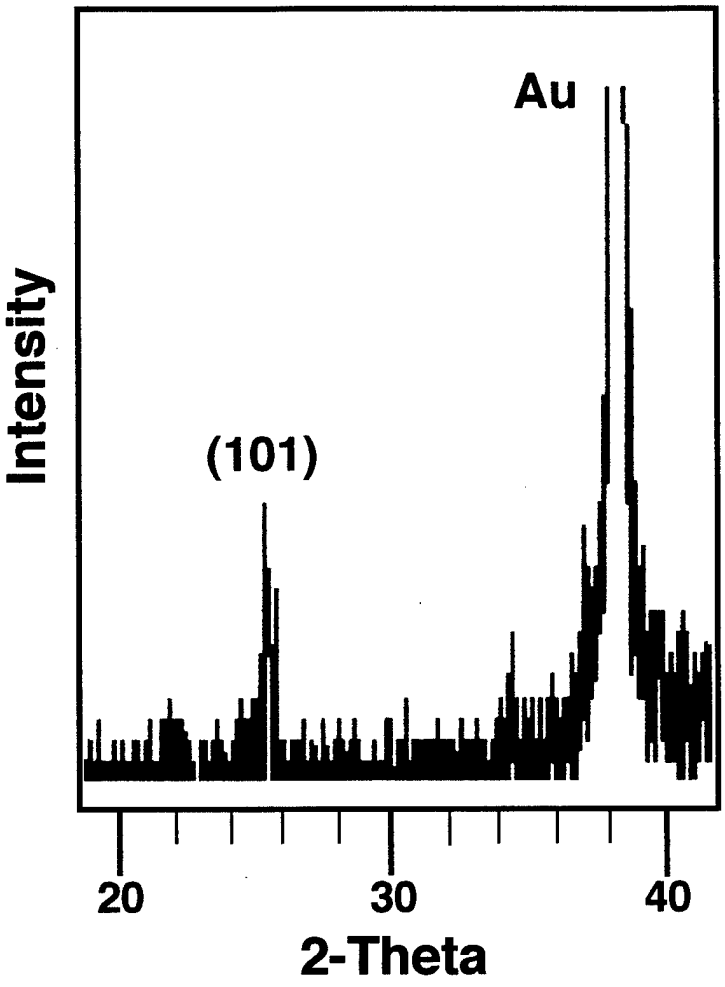


Fig 11C

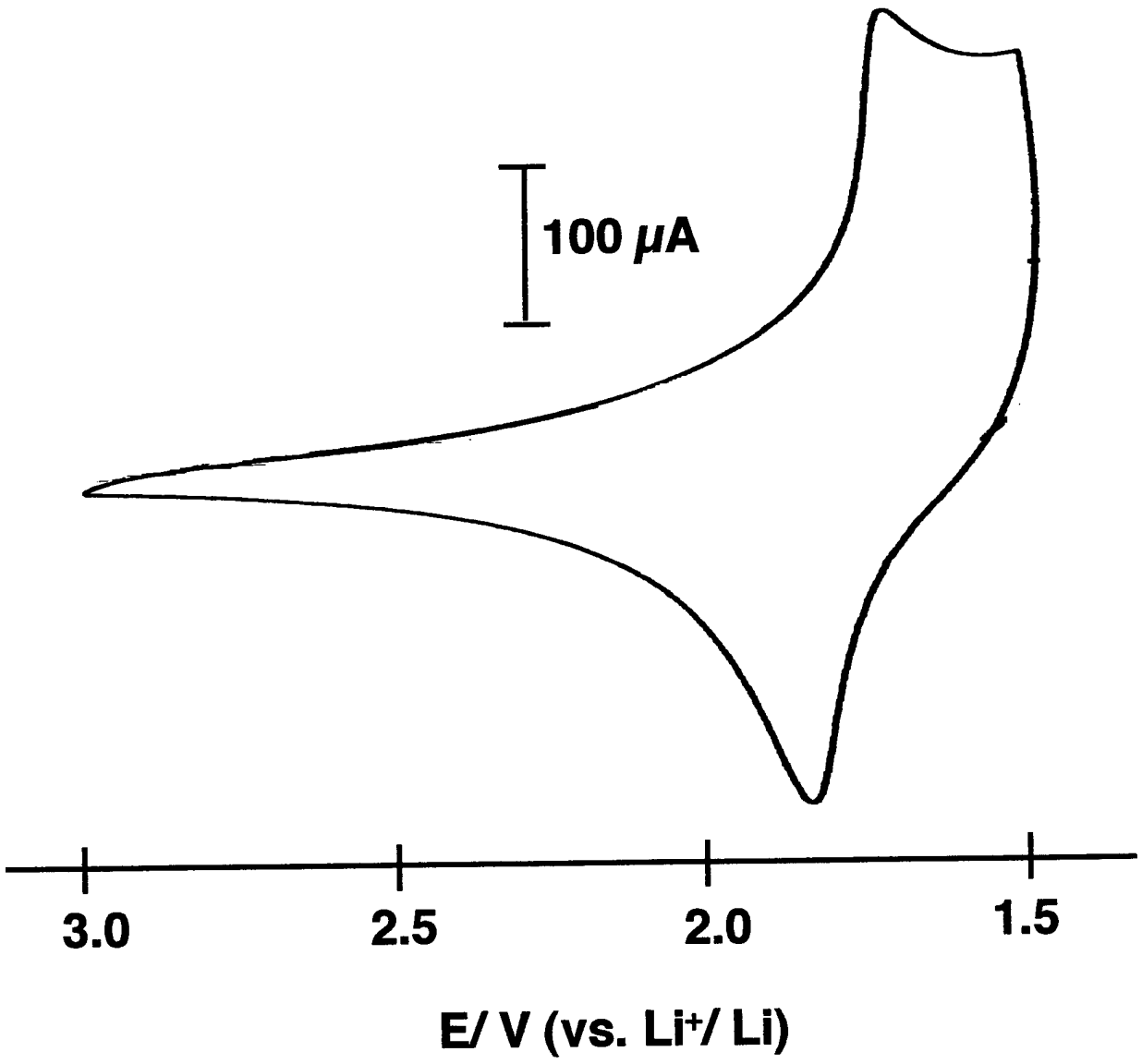
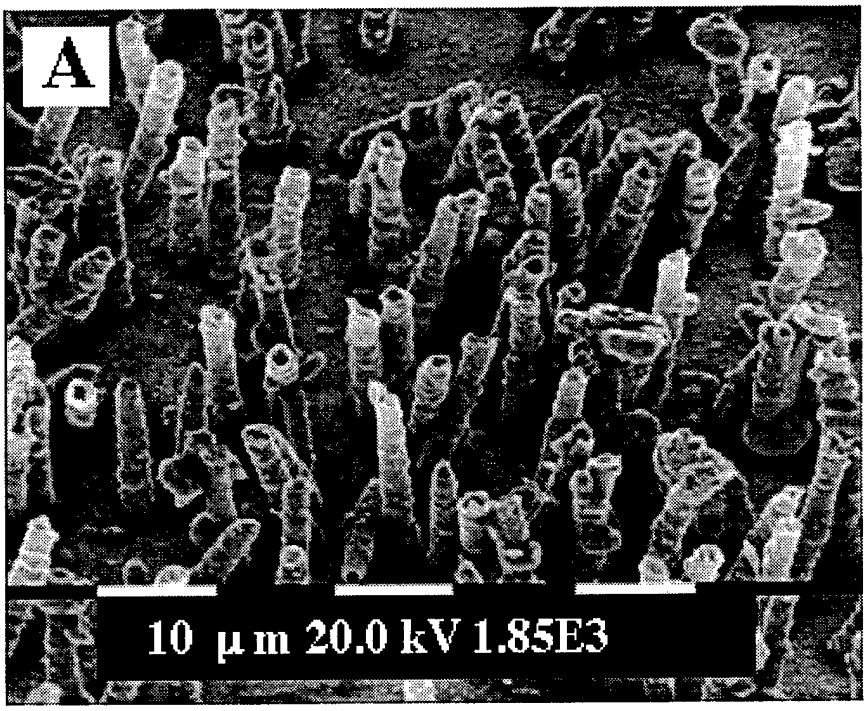


Fig 11D



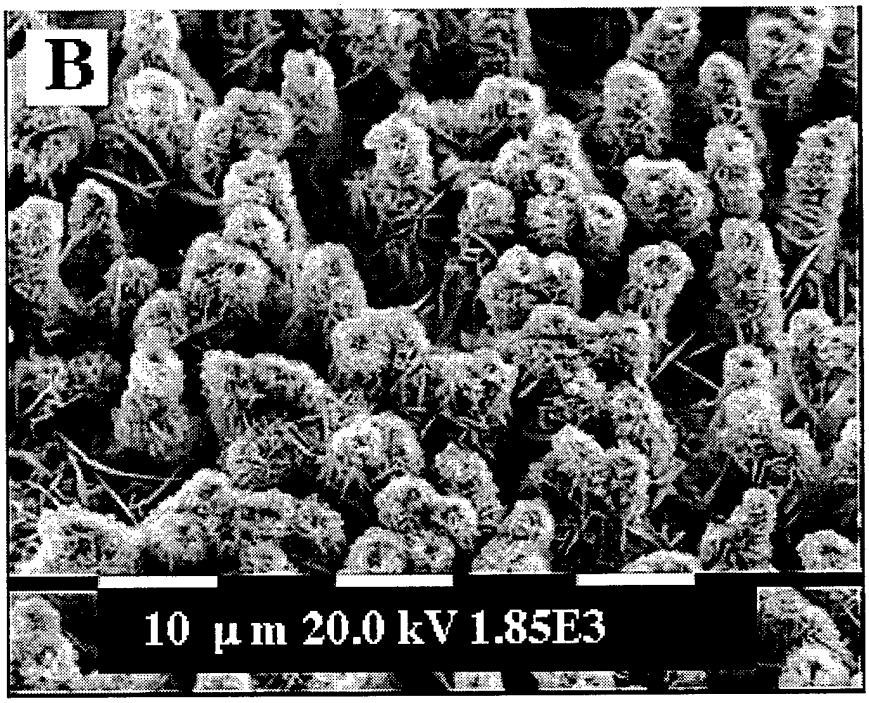


Fig 12

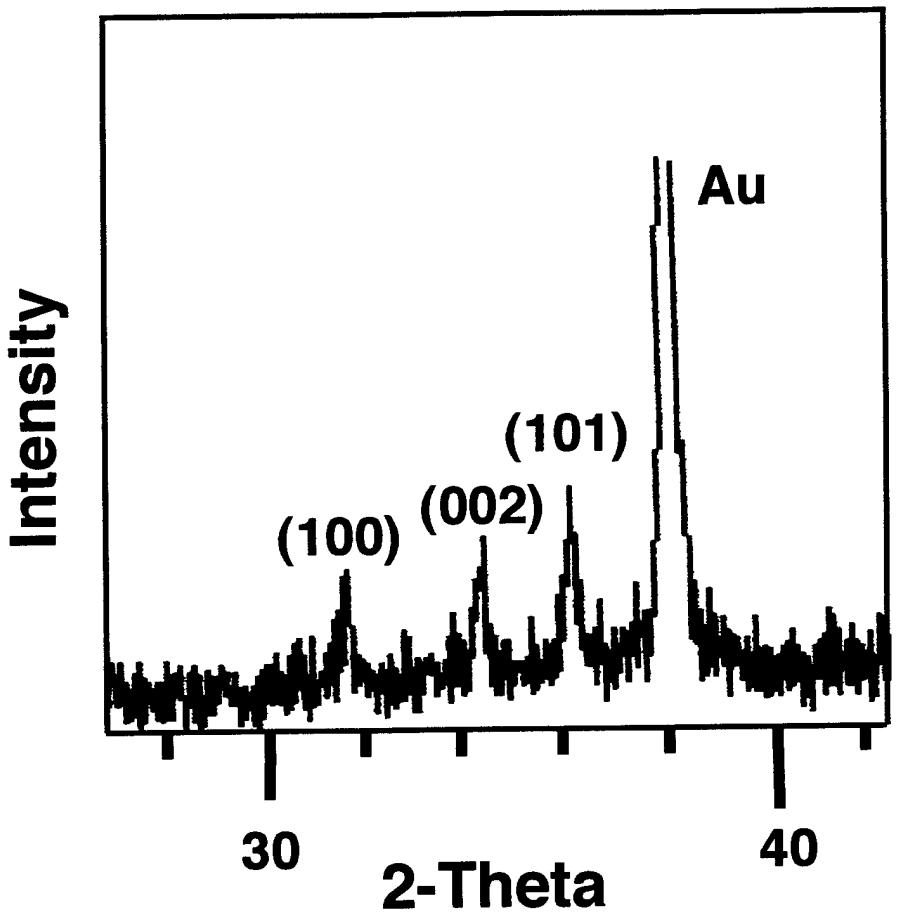


Fig 12C